

Review of Dispersants used in Response to the Deepwater Horizon Oil Spill

Scott A. Stout, Ph.D.
NewFields Environmental Forensics Practice, LLC, Rockland, MA
August 2015

Abstract

This study compiles information available on the volumes and chemical compositions of two chemical dispersants used in response to the *Deepwater Horizon* oil spill. In addition, results of chemical analysis of neat and the laboratory-prepared water soluble fractions (WSFs) of the dispersants are presented. Key findings are:

- Between April 22 and July 19, 2010 nearly 1.9 million gallons of two dispersants, Corexit 9500 (~88%) and 9527 (~12%), were used in response to the spill.
 - ~1.07 million gallons of the two formulations were applied to surface waters, mostly within 50 miles of the wellhead and reportedly not near shorelines, and
 - ~0.77 million gallons of Corexit 9500 (only) was injected at ~1500 m deep, proximal to the wellhead.
- Corexit 9500 and 9527 contain the same surfactants and stabilizer, but different solvents.
 - Sodium dioctyl sulfosuccinate (DOSS) is the main anionic surfactant in both formulations (10 to 30 wt%),
 - Propylene glycol is the stabilizer found in both formulations (1 to 5 wt%),
 - 2-butoxyethanol is the solvent in Corexit 9527 (30 to 60 wt%), and
 - a hydrotreated petroleum distillate (C₉-C₁₄) and di(propyleneglycol)-n-butyl ether isomers (DPnBs) comprise the solvent in Corexit 9500 (10 to 30 wt%).
- Various mass loadings are calculated, but in total between ~0.67 and 2.0 million kg of DOSS, and 0.07 and 0.33 million kg of propylene glycol, and 0.24 and 0.49 million kg of 2-butoxyethanol were introduced to the Gulf of Mexico (GoM) by the use of dispersants.
- Chemical analysis of neat Corexits via conventional GC and GC/MS (as per the NRDA Analytical Quality Assurance Plan (AQAP, NOAA 2014) shows they contain low concentrations of targeted hydrocarbons, the most abundant of which are C₁- to C₄-decals. Because these hydrocarbons are also present in the Macondo oil, their detection in water samples from the GoM does not necessarily reveal the presence of dispersant.
- Chemical analysis of the WSFs of Corexits identified three water soluble “marker chemicals” that can be used to recognize the presence of dispersant in water samples collected during and after the DWH oil spill. Specifically,
 - 2-butoxyethanol may indicate an impact by Corexit 9527,
 - DPnBs (a.k.a. glycol ether isomers) may indicate an impact by Corexit 9500, and
 - bis-(2-ethylhexyl)fumarate, a DOSS-derived marker, may indicate an impact by either formulation.

Based on these results, beginning in July 2010 these three “marker compounds” were incorporated into the NRDA AQAP and used in analyzing water samples from the GoM.



Concentrations reported from these analyses are considered as estimates but useful in recognizing waters apparently impacted with Corexit dispersant(s).

Introduction

Dispersants are chemical agents used to reduce the interfacial tension between oil and water. This reduction serves to enhance the formation of small(er) oil droplets that are more readily dispersed within the water column, as opposed to coalescing oil droplets that form surface slicks. The dispersed oil is expected to have a different environmental fate than any coalesced oil due to enhanced dissolution and biodegradation (owing to a smaller droplet's larger surface area-to-volume), and sedimentation upon interaction with suspended particulates (NRC, 2005).

Because dispersants are themselves mixtures of chemicals (solvents and surfactants) – sometimes proprietary – it is important to understand their compositions as a basis to assess what potential impact the dispersant themselves may have on natural resources. Identifying and measuring any dispersant-derived chemicals in the environment also provides a means to assess the spatial distribution of resources potentially impacted.

In this report, the types, volumes, and chemical compositions of the dispersants used in response to the *Deepwater Horizon* (DWH) oil spill are reviewed. The compositions of dispersants used are summarized from the available Material Safety Data Sheets (MSDSs; Attachment 1) and from chemical analysis on the neat (pure) dispersants performed herein. In addition, the neat dispersants were used to generate water soluble fractions (WSFs) in laboratory benchtop experiments, which were also chemically analyzed as a means to identify “marker chemicals” suitable for recognizing the presence of dispersants in Gulf of Mexico (GoM) water samples collected during and after the DWH oil spill.

Dispersant use during the Deepwater Horizon Oil Spill

Types of Dispersants Used

Two dispersants were used in response to the *Deepwater Horizon* oil spill, viz., Corexit EC9527A and Corexit EC9500A, hereafter simply referred to as Corexit 9527 and 9500. Corexit 9527 was developed in the 1980s and Corexit 9500 was developed in the 1990s (George-Ares and Clark 2000). Both products are currently produced by Nalco Energy Services, L.P. (Nalco; Sugarland, TX).

Both Corexit formulations contain a mixture of nonionic surfactant, anionic surfactant, solvent and a stabilizer (Singer et al. 1991; NRC 2005). The same surfactants and stabilizer are found in both Corexit 9500 and 9527. The major nonionic surfactants are ethoxylated sorbitan mono- and trioleates (Tween-80 and Tween-85) and sorbitan monooleate (Span-80) and the major anionic surfactant is sodium dioctyl sulfosuccinate (DOSS; Fig. 1; USEPA 2010). Both formulations contain the same propylene glycol stabilizer.

The major difference between the two Corexit formulations lies in the solvents used (NRC 2005). The original formulation, Corexit 9527, uses 2-butoxyethanol as a solvent (Fig. 1) whereas Corexit 9500 uses di(propylene glycol)-n-butyl ether (DPnB; Fig. 1) and a light hydrotreated petroleum distillate (commercial name, Nopar 13) as a solvent (Varadaraj et al. 1995).



Although the major chemicals present in Corexit are known, their concentrations are considered proprietary. Nalco's MSDSs for Corexit 9500 and 9527 (Attachment 1)¹ indicate both formulations contain between 10 and 30 wt% of a proprietary organic sulfonic salt (i.e., DOSS). A recent study determined that neat samples of Corexit 9500 and 9527 contained 10 wt% and 17 wt% of DOSS (Kujawinski et al 2011), which are within the range (10-30 wt%) reported on Nalco's MSDSs. The MSDSs (Attachment 1) also show that both formulations contain between 1 and 5 wt% propylene glycol. Corexit 9500 contains 10 to 30 wt% of the light hydrotreated petroleum distillate (i.e., Nopar 13) and Corexit 9527 contains between 30 and 60 wt% 2-butoxyethanol.

Volume and Locations of Dispersants Used

Between April 22 and July 19, 2010, nearly 1.9 million gallons (1,844,297 gal.) of dispersant were used in response to the DWH oil spill (BP 2014). Dispersants were used both at the sea's surface (~1.07 million gallons) and also in the subsea at a depth of ~1500 m (~0.77 million gallons) near the well head/broken riser tube. These amounts are the largest volume of dispersants ever used in response to an oil spill and is the first time dispersant has been used at depth to disperse oil (Gray et al. 2014).

The daily surface and subsea use of dispersants varied over this time period as shown in Figure 2. As can be seen, the application of dispersant to surface water was highly variable but dominated dispersant use during the first month of the spill. Subsea application of dispersant was used only intermittently prior to May 15, after which time the subsea injection was relatively consistent and dominated the dispersant use until the well was capped July 15, 2010.

Surface Use:

BP (2014) reports about 1,073,025 gallons of dispersants were applied to surface waters of the Gulf of Mexico. Most of this (~91%) was applied through aerial spraying with the balance (~9%) being applied by source control vessels. The typical rate of dispersant application to surface water was on the order of 5 gallons/acre (John Brown, Exponent, personal communication, April 2011).

Both Corexit formulations were applied to the surface water. Corexit 9527 was applied between April 22 and May 22 and Corexit 9500 was applied between April 27 and July 19. As such, the majority (~80% or 858,356 gallons) of the dispersant applied to surface water was the Corexit 9500 formulation, the balance (~20% of 214,669 gallons) being comprised of Corexit 9527. This disparity in the use of the two formulations was reportedly because the available stockpiles of Corexit 9527 were exhausted by mid-May (its last use was May 22, 2010), after which time Corexit 9500 was used exclusively for aerial application.

Figure 3 shows the aerial extent of dispersants applied to surface waters from vessels and aircraft (BP 2014). As can be seen most dispersants were applied within approximately 50 miles of the wellhead although some applications were over 100 miles from the wellhead. No dispersants were reportedly used proximal to shorelines.

Subsea Use:

BP (2014) reports about 771,272 gallons of Corexit 9500 (only) was injected subsea directly into the oil and gas plume exiting the wellhead. Its use occurred between April

¹ http://www.nalcoesllc.com/nes/documents/MSDS/NES-LLC-COREXIT-EC9500A-March_2012.pdf and http://www.nalcoesllc.com/nes/documents/MSDS/NESLLC-COREXIT-EC9527A-March_2012.pdf. Accessed in March 2012.



30 and July 15, with most being injected after May 15, 2010 (Fig. 2). Dispersant was injected to the emerging petroleum at a rate that ranged from 2.2 gallons/min to 12.1 gallons/min, with a daily average of 8.8 gallons/min.

Samples and Analyses

Neat Corexit Study

Samples of neat Corexit 9500 and 9527 were provided to NOAA by BP through Entrix and TDI-Brooks. A description of these samples is given in Table 1. It is believed these samples were collected from containers used in response to the oil spill - and not directly from Nalco. The samples were shipped under full chain-of-custody from TDI-Brooks Laboratory (College Station, Texas) to Alpha Analytical Laboratory (Alpha; Mansfield, Massachusetts) on May 26, 2010 and were safely received on May 28, 2010. The samples were analyzed in accordance with the NOAA (2014) Analytical Quality Assurance Plan (AQAP) via:

- (1) *TEM and Selected Hydrocarbon (SHC) Quantification and Fingerprinting:* a modified EPA Method 8015B was used to determine the concentration of total extractable materials (TEM; C₉-C₄₄) and concentrations of *n*-alkanes (C₉-C₄₀) and selected (C₁₅-C₂₀) acyclic isoprenoids (e.g., pristane and phytane), and simultaneously provide a high resolution gas chromatography-flame ionization detection (GC/FID) fingerprint of the samples. Following solvent extraction with dichloromethane (DCM) the sample extracts were spiked with appropriate internal standards and surrogates and analyzed by GC/FID. There was no silica gel cleanup of the extract performed. The concentrations of target compounds in the dispersants are reported in mg/kg_{dispersant} and are surrogate corrected.
- (2) *PAH, Alkylated PAH and Petroleum Biomarkers:* Semi-volatile compounds in each dispersant were analyzed using GC/MS via a modified EPA Method 8270. This analysis provided the concentration of (1) approximately 80 PAH, alkylated PAH homologues, individual PAH isomers, and sulfur-containing aromatics and (2) approximately 50 tricyclic and pentacyclic triterpanes, regular and rearranged steranes, and triaromatic steroids. The concentrations of target compounds in the dispersants are reported in mg/kg_{dispersant} and are surrogate corrected.

In addition, each of the neat Corexit samples was analyzed using full scan GC/MS in order to obtain mass spectral data on non-target analytes. These data were evaluated with the intention of identifying a suite of compounds in the Corexit formulations that might be used to monitor the presence of Corexit in environmental matrices.

Corexit Water-Solubility Study

As a means to assess which "marked chemicals" derived from Corexit might be anticipated to occur in waters of the GoM, benchtop experiments were performed at Alpha to obtain the water soluble fraction (WSF) of Corexit 9500 and 9527 using the method based on Shui et al. (1990). Briefly, 1L stock of 32 ppt artificial seawater was prepared by adding 32 grams of *Instant Ocean* to 1L of distilled water. The WSFs were then prepared by gently casting 2.5 mL of neat Corexit 9500 or 9527 atop 100 mL of



artificial seawater in a 125 mL separatory funnel with and periodically gently swirling the funnel over 48 hours at 25°C. During the initial spiking, the neat Corexit was gently cast onto the surface of the water so as to not entrain the Corexit into the water. The WSF of each Corexit formulation was prepared in duplicate, along with a seawater blank (Table 2). The seawater (79-91 mL) from each funnel was then slowly drained and analyzed using the TEM and PAH methods described above.

The TEM, SHC, PAH and biomarker data for the neat Corexit samples and their WSFs were all reported through NOAA's data management system protocols and are available in the DIVER data warehouse.

Results and Discussion

Composition of Neat Corexit

The Corexit 9500 and Corexit 9527 formulations were determined to contain 426,000 µg/g (42.6 wt%) and 397,000 µg/g (39.7 wt%) TEM (C₉-C₄₄), respectively. This indicates that approximately 60% of the mass of these dispersants was too polar and/or too large in molecular weight to be detected by conventional GC/FID. This result is not unexpected since the dispersants are known to contain multiple surfactants with high molecular weights or polarities (see above, Attachment 1; Fig. 1).

Although not individually quantified, most of the chromatographable mass of the TEM occurs in a few dominant peaks (Fig. 4). The identification of these peaks was achieved through a combination of mass spectral library search based upon the full scan GC/MS analysis of the neat Corexit formulations, knowledge about the chemicals known to be present in the dispersants (US EPA, 2010), as well as information provided by Nalco chemists.² The major compounds identified in the Corexit samples are provided in the key to Figure 4.³

The Corexit 9500 contains a prominent petroleum component spanning the C₉-C₁₄ boiling range that is dominated by a small unresolved complex mixture (UCM), which appears as a 'hump' in the chromatogram (Fig. 4A). This petroleum is the light hydrotreated petroleum distillate (Nopar 13) identified in Nalco's MSDS for Corexit 9500. Hydrotreatment is a refining process that tends to convert aromatic hydrocarbons into aliphatic hydrocarbons (e.g., naphthalenes are converted to decalins). Therefore, this petroleum component is not anticipated to contain abundant aromatic hydrocarbons (although some alkylated naphthalenes were detected; see below).

Full scan GC/MS analysis conducted on the neat Corexit 9500 revealed that n-alkanes and n-alkyl-cyclohexanes are absent from the distillate. The resolved peaks (excluding Peak #3, see below) were identified as various C₁₁ to C₁₆ isoparaffins (branched

² Timothy P. McGinnis et al. (email to Rob Barrick, June 9, 2010).

³ Sporadic detections of individual targeted n-alkanes were reported by Alpha, and corresponding concentrations were reported to NOAA's data management. However, these detections are attributed to non-n-alkanes that share retention time with n-alkanes. GC/MS confirmed the absence of true n-alkanes. For example, Alpha reported the presence of n-C₂₉ in Corexit 9527, which is actually the first peak #8 (a branched chain ester) seen in Fig. 4B. Therefore, the SHC concentrations that exist within DIVER are not reported herein and should be used with great caution.



alkanes), the largest of which was tentatively identified as 3-methyl-5-propyl nonane (Peak 9 in Fig. 4A).

Peak #3 (Fig. 4A) is actually comprised of three closely-eluting peaks identified as isomers of di(propyleneglycol)-n-butyl ethers (DPNBs), which are known components in the Corexit 9500's solvent. (The mass spectrum for DPNBs is presented later in this report; Fig. 7.)

As expected, the dominant solvent found in Corexit 9527 was identified as 2-butoxyethanol (Peak #1; Fig. 4B). Unexpectedly however, the Corexit 9527 also contains some petroleum distillate (Fig. 4B), which is visible as a very small UCM in the C₉-C₁₄ boiling range (Fig. 4B). The presence of petroleum distillate was supported by the full scan GC/MS analysis of the neat Corexit 9527, which for example, also identified numerous isoparaffins including 3-methyl-5-propyl nonane (Peak #9 in Fig. 4). This is unexpected because Corexit 9527 is not supposed to contain a petroleum distillate solvent. It is possible, however, that the neat sample of Corexit 9527 provided by BP was cross-contaminated with a trace amount of Corexit 9500 at some time during its handling prior to the collection of the sample.

Table 3 provides the concentrations of PAHs and related compounds measured in the neat Corexit formulations. Inspection reveals that Corexit 9500 contains a series of alkylated decalins that increase in concentration with increasing degree of alkylation (Table 3). Somewhat lower concentrations of alkylated decalins were also present in the Corexit 9527 (Table 3). Total concentrations of C₁ to C₄-decalins in Corexit 9500 and 9527 were 156 and 85 mg/kg, respectively.

Decalins are decahydronaphthalenes, i.e., two-ring aliphatic hydrocarbons. Their presence in the Corexit formulations is likely attributable to the hydrotreated C₉-C₁₄ petroleum solvent component that was prominent in Corexit 9500 and present in trace amounts in Corexit 9527 (see above; #5 in Fig. 4). Their origin may, at least in part, lie in the hydrogenation of alkylated naphthalenes during hydrotreatment.

Not all naphthalene species, however, are removed/destroyed in the hydrotreated petroleum solvent. Both Corexit formulations also contained detectable concentrations of methyl-naphthalene isomers, as well as biphenyl (Table 3). Corexit 9500 contained 1.9, 1.3, and 23 mg/kg of 2-methyl naphthalene, 1-methyl naphthalene, and biphenyl, respectively, while Corexit 9527 contained 10.0, 6.9, and 6.0 mg/kg, respectively (Table 3).⁴

DOSS

DOSS is too large and too polar of a compound (Fig. 1) to be detected using conventional GC. Liquid chromatography (LC) is more appropriate for direct analysis of DOSS and has been widely used in the analysis of waters from the Gulf of Mexico (Place et al. 2010; Gray et al. 2010, 2014; Kujawinski et al. 2011; Mathew et al. 2012; Ramirez et al. 2013; White et al. 2014; Place et al. 2014).

⁴ The concentrations of individual methyl-naphthalene isomers exceed the C₁-naphthalene concentrations because of response factor differences; C₁-naphthalene uses the response factor (RF) of naphthalene while the individual isomers use authentic RFs.



Conventional GC however, can prove useful in recognizing the presence of DOSS. Specifically, conventional GC shows that both formulations contain a prominent peak determined to be bis-(2-ethylhexyl)fumarate (Peak 7; Fig. 4). (The mass spectrum for this compound is presented later in this report; Fig. 7.) This compound and the corresponding bis-(2-ethylhexyl)maleate (Peak 6) are reported to be primary thermal degradation (desulfonation) products of DOSS (Asano, 1981). Nalco chemists² confirmed that DOSS has been shown lose a sulfonic acid group and convert to diesters of fumaric and maleic acid upon heating (Fig. 5), such as is experienced in the heated injection port of a GC. Because of its *trans* configuration, the fumarate ester is thermodynamically favored, and thus forms preferentially leading to the prominent peak in the chromatograms of both Corexit formulations (Peak 7 in Fig. 4). Nalco chemists contend that the specific heating conditions (injection port temperature and oven heating) are likely to affect the absolute and relative abundances of the two diesters formed. This phenomenon would likely confound any attempt at absolute quantification of these compounds via conventional GC – as a proxy for quantifying DOSS directly – in authentic samples (see below). However, the detection of these diesters in authentic samples analyzed by conventional GC methods are useful qualitative indicators of DOSS' presence in authentic field samples (see below).

Microbial desulfonation reportedly can sometimes occur (Cook et al. 1999). Therefore, it is at least possible that biodegradation of DOSS could produce fumaric and maleic acid derivatives. Whether or not microbial desulfonation may have happened in Gulf of Mexico waters (or only thermal desulfonation within GC injection ports) is currently unknown.

Estimated Mass Loading of Corexit and Corexit-Derived Chemicals to the Gulf of Mexico

The volumes (gallons) of dispersants reportedly used in response to the DWH oil spill (BP, 2014) can be converted into mass (kg) using the density of the Corexit formulations obtained from their MSDSs (Attachment 1). This calculation is made at the top of Table 4, which show approximately:

- 813,058 kg of Corexit 9527 was applied at the surface,
- 3,079,709 kg of Corexit 9500 was applied at the surface, and
- 2,767,259 kg of Corexit 9500 was injected to the subsurface.

In total, 6,660,026 kg of dispersant was added to the Gulf of Mexico waters.

The compositional data contained in the Corexit MSDSs (Attachment 1) can be used to calculate the approximate masses of individual Corexit-derived chemicals added to Gulf of Mexico waters. Table 4 shows that the minimum and maximum concentrations of selected chemicals present in each Corexit formulation, as obtained from the MSDSs (Attachment 1). For example, both Corexit formulations contain between 10 and 30 wt% of DOSS (or 100,000 to 300,000 mg/kg; Table 4). Given the calculated masses of dispersant used, between:

- 243,917 and 487,835 kg of 2-butoxyethanol,
- 666,003 and 1,778,482 kg of DOSS,
- 66,600 and 333,001 kg of propylene glycol, and
- 584,697 and 1,754,090 kg of petroleum distillate



were added to waters of the GoM due to use of dispersants during the response to the DWH oil spill.⁵

The concentrations of selected semi-volatile chemicals detected in the neat Corexits (Table 3) can also be used to estimate that:

- 975 kg of C₁ to C₄-decalins,
- 19 kg of 2-methylnaphthalene,
- 13 kg of 1-methylnaphthalene,
- 139 kg of biphenyl, and
- 90 kg of C₂ to C₄-naphthalenes

were added to waters of the Gulf of Mexico due to use of dispersants. Although not presented herein, by comparison the relative mass of these five hydrocarbons from the use of dispersant represents only extremely small percentages (0.01 to 0.45 wt%) of the total mass of each introduced from the Macondo oil itself.

Water Soluble Fraction (WSF) of Corexit Formulations

The concentration of TEM recovered from the four WSFs narrowly ranged from 4110 and 4730 mg/L of TEM (Table 5). The TEM concentrations measured are well below the concentrations that were added to the seawater during laboratory preparation of the WSFs, which were on the order of 25,000 to 27,500 mg/L.⁶ This means that the TEM concentrations measured in the WSFs represent only ~20% of the Corexit originally cast onto the seawater, dissolved into the underlying water phase, recovered, and measured as TEM. This may seem to be a low recovery, but as demonstrated by the analysis of the neat Corexit, only about 40% of the mass of these formulations were chromatographable by conventional GC (see above). Thus, recovery of ~20% of the mass of the spiked Corexit from the WSF indicates that about half of the Corexit spike was dissolved into the water. This recovery of about half the total chromatographable mass (i.e., ~20% of 40%) would seem consistent with the observation that a floating film (white cloudy layer) of dispersant was visible at the surface of the water at the completion of the 48 hours. This film is believed to represent Corexit that had emulsified but not dissolved into the underlying water – and this film apparently represented about half of the mass spiked.

The GC/FID chromatograms for TEM comprising the WSFs of Corexit 9500 and 9527 are shown in Figure 6. The WSF of the Corexit 9500 is overwhelmingly comprised of the DPNB isomers (Peak #3). Trace amounts of 2-ethylhexanol (Peak #2) and bis-(2-ethylhexyl)fumarate (Peak #7) are also present (Fig. 6A). The Corexit 9500 WSF does not contain any obvious petroleum distillate (solvent; Fig. 6A), which was prominent in the neat Corexit 9500 (Fig. 4A). This suggests the hydrocarbons within the petroleum distillate did not readily partition into the seawater.

⁵ If, instead of using the MSDS ranges of 10-30 wt% DOSS in both formulations, the measured concentrations of DOSS reported by Kujawinski et al. (2011) are used (i.e., 10 and 17 wt% in Corexit 9500 and 9527, respectively), the total DOSS mass loading is 722,917 kg (446,191 kg to the surface and 276,726 kg to the subsurface).

⁶ Corexit 9500 and 9527 have densities of ~1.1 g/ml and 1.0 g/ml, respectively (Nalco MSDS). Thus, 2.5 ml of Corexit in 100 ml of seawater corresponds to a concentration of 27,500 and 25,000 mg/L if all of the dispersant were to enter the water, be recovered upon extraction, and be analyzed as TEM.



The WSF of Corexit 9527 contains predominantly 2-butoxyethanol (Peak #1) with lesser amounts of 2-ethylhexanol, 2-(2-butoxyethoxy)ethanol, bis-(2-ethylhexyl) maleate, and bis-(2-ethylhexyl)fumarate (Peak #'s 2, 4, 6, and 7, respectively; Fig. 6B).

Application of WSF Results - Corexit "Marker Compounds"

Based upon the WSF results, three prominent compounds in the neat Corexit formulations and their WSFs – viz., Peaks 1, 3 and 7 (Figs. 4 and 6) – are suitable for use as "marker compounds" for monitoring the presence of Corexit dispersants in water samples from the Gulf of Mexico. The three marker compounds are:

- 2-butoxyethanol (Peak #1 in Fig. 4B and 6B) as a suitable marker for Corexit 9527,
- di(propyleneglycol)-n-butyl ethers (DPnBs)⁷, which appear as three closely-eluting isomers reported together as a single analyte (Peak #3 in Fig. 4A and 6A) as a suitable marker for Corexit 9500, and
- bis-(2-ethylhexyl)fumarate (Peak #7 in Fig. 4 and 6) as a suitable marker for DOSS derived from both Corexit 9500 and 9527.

The mass spectra and adopted primary quantification and secondary confirmation ions for these three marker compounds are shown in Figure 7.

Absolute quantification of these marker compounds in water samples was not pursued as part of the NRDA for samples analyzed by Alpha Laboratory. The reasons for this included the difficulty of obtaining authentic standards for the DPnB isomers and bis-(2-ethylhexyl)fumarate, the potential for these highly polar compounds to remain "stuck" to glassware, and the variability likely imparted due to varying degrees of thermal breakdown of DOSS during GC analysis (see above).

However, the WSF results confirm that these three Corexit marker compounds can be recovered using conventional liquid-liquid extraction techniques and identified using conventional GC/MS-SIM. Therefore, these compounds' presence can be recognized and their concentrations can be estimated (but not absolutely quantified; see below). As such, in July 2010 these compounds' mass spectral (primary and secondary) ions (Fig. 7) were incorporated into Alpha Laboratory's modified EPA Method 8270 analysis, which was subsequently incorporated into the AQAP for the qualitative analysis of Corexit marker compounds waters. The method was not appropriate for soils, sediments or tissues due to the need to clean-up these matrices' extracts using silica gel in order to remove polar compounds. Silica gel treatment would undoubtedly remove these polar Corexit marker compounds. Therefore, Alpha did not attempt to recognize the presence of Corexit marker compounds in soils, sediments or tissues throughout the analysis of NRDA samples. Because oils (e.g., tarballs) were not treated with silica gel, occasionally oils were analyzed for the Corexit markers.

The estimated concentration of the three Corexit marker compounds in waters was achieved by integrating the appropriate peaks, assuming a response factor of 1, and calculating an estimated concentration of each in the water samples analyzed. These concentrations were reported as "T" qualified (i.e., T = tentatively identified Corexit

⁷ These compounds are reported as "glycol ether isomers" by Alpha. Battelle reported the concentration of these three isomers as "DPnB".



compound), which distinguishes these from “E” (estimated) or “J” qualified data for other analytes. The Corexit marker compound concentrations were reported in separate Form I data summaries (i.e., separate from the alkylated PAH Form I data summary) for the Gulf of Mexico water samples analyzed for these compounds. There was no surrogate correction performed for the marker compound’s concentrations.

This method of quantification is demonstrated in the analysis of the WSFs of Corexit 9500 and 9527 prepared in this study. Table 5 shows that, as would be anticipated,

- Duplicate WSFs of Corexit 9500 contained relatively high concentrations of DPnBs ($1,450 \pm 255$ mg/L; avg. $\pm \sigma$).
- Duplicate WSFs of Corexit 9527 contained relatively high concentrations of 2-butoxyethanol (389 ± 21 mg/L; avg. $\pm \sigma$).
- Duplicate WSFs for both Corexit formulations contained relatively consistent but lower concentrations of the DOSS breakdown compound (bis-(2-ethylhexyl)fumarate; 1.12 ± 0.15 mg/L).

As would be anticipated based upon its purported composition, there was virtually no 2-butoxyethanol detected in the WSFs for Corexit 9500 (Table 5). Contrary to its purported composition, there was a trace concentration of DPnBs unexpectedly detected in the WSFs for Corexit 9527 (Table 5). The trace of DPnBs in the Corexit 9527 WSFs may be due to a trace amount of Corexit 9500 that appears to have been present in the neat Corexit 9527 sample provided (i.e., recall the neat Corexit 9527 contained some petroleum distillate not expected to be present in this formulation; Fig. 4B). Therefore, a trace amount of Corexit 9500 appears to have cross-contaminated the Corexit 9527 sample provided for this study.

The estimated concentrations of these three Corexit marker compounds in authentic water samples from the Gulf of Mexico can be used as indicators for the presence of Corexit dispersant(s).

Because Corexit 950 was the only dispersant injected at the wellhead (BP, 2014) one would expect that detection of its marker compounds, viz., DPnBs and (bis-(2-ethylhexyl)fumarate, in deep sea water samples (e.g., Kujawinski et al., 2014; Grey et al., 2014) or deep surface sediments and corals (e.g., White et al., 2014) can be confidently attributed to Corexit 9500’s use at the wellhead. The detection of DPnBs or (bis-(2-ethylhexyl)fumarate in pelagic surface water would also seem reasonably attributed to surface applications of Corexit 9500. Similarly, detection of 2-butoxyethanol or (bis-(2-ethylhexyl)fumarate in pelagic surface water would also seem reasonably attributable to surface application of Corexit 9527. However, more caution seems appropriate for interpreting the detection/presence of any of these marker compounds in nearshore and inland waters in urbanized areas, where alternate (non-Corexit) sources may exist (Hayworth and Clement, 2012).

References

Asano, S., 1981. "Analysis of dialkyl sulfosuccinate by pyrolysis gas chromatography". Kanzei Chuo Bunsekishoho, 22: 23 – 27.

BP, 2014. "Gulf Science Data Reference Oil Characterization Data". Website: <http://gulfsciencedata.bp.com/>, directory: Other; subdirectory: Dispersant Application;



filename: DispersantApplication_OTH-02v01-01.xlsx and DispersantApplication_OTH-02v01-02.xlsx. Last accessed January 24, 2014.

Cook, Alasdair M., Heike Laue, and Frank Junker, 1999. "Microbial desulfonation". *FEMS Microbiol. Rev.* 5: 399-419.

George-Ares, A. and J.R. Clark, 2000. "Aquatic toxicity of two Corexit dispersants". *Chemosphere* 40: 897-906.

Gray, James L., Leslie K. Kanagy, Edward T. Furlong, Jeff W. McCoy, and Chris Kanagy, 2010. "Detection of the anionic surfactant di(ethylhexyl)sodium sulfosuccinate in water samples collected from Gulf of Mexico coastal waters before and after landfall of oil from the Deepwater Horizon oil spill, May to October, 2010". U.S.G.S. Open File Report 2010-1318;

Gray, James L., Leslie K. Kanagy, Edward T. Furlong, Chris Kanagy, Jeff W. McCoy, Andrew Mason, and Gunnar Lauenstein, 2014. "Presence of the Corexit component dioctyl sodium sulfosuccinate in Gulf of Mexico waters after the 2010 Deepwater Horizon oil spill". *Chemosphere* 95: 124-130.

Hayworth, Joel S., and T. Prabakhar Clement, 2012. "Provenance of Corexit-related chemical constituents found in nearshore and inland Gulf Coast waters". *Marine Pollution Bulletin* 64: 2005-2014.

Kujawinski, Elizabeth B., Melissa C. Kido Soule, David L. Valentine, Angela K. Boysen, Krista Longnecker, and Molly C. Redmond, 2011. "Fate of dispersants associated with the Deepwater Horizon oil spill". *Environ. Sci. Technol.* 45: 1298-1306.

Mathew, Johnson, David L. Schroeder, Lawrence B. Zintek, Caitlin R. Schupp, Michael G. Kosempa, Adam M. Zachary, George C. Schupp, and Dennis J. Wesolowski, 2012. "Dioctyl Sulfosuccinate Analysis in Near-Shore Gulf of Mexico Water by Direct-Injection Liquid Chromatography Tandem Mass Spectrometry". *Journal of Chromatography A* 1231:46-51.

National Research Council, 2005. "Oil spill dispersants: Efficacy and Effects". *The National Academies Press*, Wash. D.C., pp. 377.

NOAA, 2014. "Analytical quality assurance plan, Mississippi Canyon 252 (Deepwater Horizon) natural resource damage assessment", Version 4.0. May 30, 2014.

Place, Benjamin J., Brian Anderson, Abdou Mekebri, Edward T. Furlong, James L. Gray, Ron Tjeerdema, and Jennifer Field, 2010. "A role for analytical chemistry in advancing our understanding of the occurrence, fate, and effects of Corexit oil dispersants". *Environ. Sci. Technol. Viewpoint*, 44: 6016-6018.

Place, Benjamin J., Matt J. Perkins, Ewan Sinclair, Adam L. Barsamian, Paul R. Blakemore, and Jennifer A. Field, 2014. "Trace analysis of surfactants in Corexit oil dispersant formulations and seawater". *Deep-Sea Res. II*, available on-line Jan. 2014.

Ramirez, Cesar E., Sudha Batchu, and Piero Gardinali, 2013. "High sensitivity liquid chromatography tandem mass spectrometric methods for the analysis of dioctyl sulfosuccinate in different stages of an oil spill response monitoring effort". *Anal. Bioanal. Chem.* 405: 4167-4175.

Shiu, Wan Ying, Mark Bobra, Alice M. Bobra, Aila Maijanen, Leena Suntio, and Donald Mackey, 1990. "The water solubility of crude oils and petroleum products". *Oil Chem. Pollut.* 7: 57-84.



Singer, Michael M., Deborah L. Smalheer, Ronald S. Tjeerdema, and Michael Martin, 1991. "Effects of spiked exposure to an oil dispersant on the early life stages of four marine species". J. Environ. Tox. Chem. 10: 1367-1374.

U.S. EPA, June 2010. Website: <http://www.epa.gov/bpspill/dispersants-qanda.html#list>.

Varadaraj, R., M.L. Robbins, J. Bock, S. Pace, and D. MacDonald, 1995. "Dispersion and biodegradation of oil spills on water". In: Proc. of the 1995 Int'l. Oil Spill Conf., Long Beach, CA, American Petroleum Institute, Wash., D.C.

White, Helen K., Shelby L. Lyons, Sarah J. Harrison, David M. Findley, Yina Liu, and Elizabeth B. Kujawinski, 2014. "Long-term persistence of dispersants following the Deepwater Horizon oil spill". Env. Sci. Technol. Letters 1: 205-299.



Table 1: Inventory of Corexit Samples Studied Herein.

| <i>Sample ID</i> | <i>Alpha Lab ID</i> | <i>Date Collected</i> | <i>Description</i> |
|-------------------------|----------------------------|------------------------------|---|
| Corexit 9500 | 1005076-01 | 05/23/2010 | Field sample from BP; provided by Entrix to TDI-Brooks |
| Corexit 9527 | 1005076-02 | 05/23/2010 | Field sample from BP; provided by Entrix to TDI-Brooks |



Table 2: Inventory of Laboratory-Produced Water Soluble Fractions (WSFs) of Corexit Samples Studied Herein.

| <i>Sample ID</i> | <i>Lab ID</i> | <i>Date Produced</i> | <i>Description</i> |
|-------------------------|----------------------|-----------------------------|-------------------------------|
| Corexit 9500 | 1007077-01 | 06/18/2010 | WSF of Corexit 9500 |
| Corexit 9500 Dup | 1007077-02 | 06/18/2010 | WSF of Corexit 9500 duplicate |
| Corexit 9527 | 1007077-03 | 06/18/2010 | WSF of Corexit 9527 |
| Corexit 9527 Dup | 1007077-04 | 06/18/2010 | WSF of Corexit 9527 duplicate |
| Seawater Blank | 1007077-05 | 06/18/2010 | Artificial Seawater blank |



Table 3: Concentrations of TEM, PAHs and related semi-volatiles in neat Corexit formulations.
All concentrations in $\mu\text{g/g}_{\text{surfactant}}$ and are surrogate corrected.

| | Corexit 9500 | | Corexit 9527 | | | Corexit 9500 | Corexit 9527 |
|--|--------------|---|--------------|---|----------------------------|--------------|--------------|
| Total Extractable Material | 426000 | | 397000 | | C1-Fluoranthenes/Pyrenes | nd | nd |
| | | | | | C2-Fluoranthenes/Pyrenes | nd | nd |
| cis/trans-Decalin | nd | | 1.4 | J | C3-Fluoranthenes/Pyrenes | nd | nd |
| C1-Decalins | 1.5 | J | 3.5 | G | C4-Fluoranthenes/Pyrenes | nd | nd |
| C2-Decalins | 19 | | 17 | | Naphthobenzothiophenes | nd | nd |
| C3-Decalins | 47 | | 38 | | C1-Naphthobenzothiophenes | nd | nd |
| C4-Decalins | 88 | | 26 | | C2-Naphthobenzothiophenes | nd | nd |
| Benzo(b)thiophene | nd | | 0.16 | J | C3-Naphthobenzothiophenes | nd | nd |
| C1-Benzo(b)thiophenes | nd | | 3.0 | | C4-Naphthobenzothiophenes | nd | nd |
| C2-Benzo(b)thiophenes | nd | | 1.4 | J | Benz[a]anthracene | nd | nd |
| C3-Benzo(b)thiophenes | nd | | 4.9 | G | Chrysene/Triphenylene | nd | nd |
| C4-Benzo(b)thiophenes | nd | | 1.4 | J | C1-Chrysenes | nd | nd |
| Naphthalene | nd | | 4.9 | | C2-Chrysenes | nd | nd |
| C1-Naphthalenes | 9.1 | G | 12 | | C3-Chrysenes | nd | nd |
| C2-Naphthalenes | 12 | | 14 | | C4-Chrysenes | nd | nd |
| C3-Naphthalenes | nd | | 7.0 | | Benzo[b]fluoranthene | nd | nd |
| C4-Naphthalenes | nd | | 3.1 | | Benzo[k]fluoranthene | nd | nd |
| Biphenyl | 23 | | 6.0 | | Benzo[a]fluoranthene | nd | nd |
| Dibenzofuran | nd | | 0.39 | J | Benzo[e]pyrene | nd | nd |
| Acenaphthylene | nd | | nd | | Benzo[a]pyrene | nd | nd |
| Acenaphthene | nd | | nd | | Perylene | nd | nd |
| Fluorene | 0.10 | J | 0.57 | J | Indeno[1,2,3-cd]pyrene | nd | nd |
| C1-Fluorenes | nd | | 0.50 | J | Dibenz[a,h]anthracene | nd | nd |
| C2-Fluorenes | nd | | nd | | Benzo[g,h,i]perylene | nd | nd |
| C3-Fluorenes | nd | | nd | | Carbazole | nd | nd |
| Anthracene | nd | | nd | | | | |
| Phenanthrene | nd | | 0.34 | J | | | |
| C1-Phenanthrenes/Anthracenes | nd | | nd | | <i>Individual Isomers</i> | | |
| C2-Phenanthrenes/Anthracenes | nd | | nd | | 4-Methyldibenzothiophene | nd | nd |
| C3-Phenanthrenes/Anthracenes | nd | | nd | | 2/3-Methyldibenzothiophene | nd | nd |
| C4-Phenanthrenes/Anthracenes | nd | | 0.31 | J | 1-Methyldibenzothiophene | nd | nd |
| Retene | nd | | 1.2 | J | 3-Methylphenanthrene | nd | nd |
| Dibenzothiophene | 0.06 | J | 0.13 | J | 2/4-Methylphenanthrene | nd | nd |
| C1-Dibenzothiophenes | nd | | nd | | 2-Methylantracene | nd | nd |
| C2-Dibenzothiophenes | nd | | nd | | 9-Methylphenanthrene | nd | nd |
| C3-Dibenzothiophenes | nd | | nd | | 1-Methylphenanthrene | nd | nd |
| C4-Dibenzothiophenes | nd | | nd | | 2-Methylnaphthalene | 1.9 | 10.0 |
| Benzo(b)fluorene | nd | | nd | | 1-Methylnaphthalene | 1.3 | J 6.9 |
| Fluoranthene | nd | | nd | | 2,6-Dimethylnaphthalene | nd | 5.7 |
| Pyrene | nd | | nd | | 2,3,5-Trimethylnaphthalene | nd | 0.60 J |
| J - estimated, below sample specific reporting limit | | | | | | | |
| G - interference contributes to concentration | | | | | | | |



Table 4: Estimated Mass Loadings of selected Corexit-derived compounds to the Gulf of Mexico from their use in response to the *Deepwater Horizon* oil spill.

| | Surface Application | | Subsurface Injection | | Total Dispersant | |
|---|---------------------|---------------------|----------------------|------------|------------------|------------|
| BP Reported Volume (Mass) | Corexit 9527 | Corexit 9500 | Corexit 9500 | | | |
| Volume Applied (gallons) | 214669 | 858356 | 771272 | | | 1844297 |
| Density (lb/gallon) | 8.35 | 7.91 | 7.91 | | | |
| Density (kg/gallon) | 3.79 | 3.59 | 3.59 | | | |
| Mass Applied (kg) | 813058 | 3079709 | 2767259 | | | 6660026 |
| | | | | | | |
| MSDS Concentrations (mg/kg) | <i>Min</i> | <i>Max</i> | <i>Min</i> | <i>Max</i> | <i>Min</i> | <i>Max</i> |
| 2-butoxyethanol | 300000 | 600000 | | | | |
| Proprietary sulfonic acid salt (DOSS) | 100000 | 300000 | 100000 | 300000 | 100000 | 300000 |
| Propylene glycol | 10000 | 50000 | 10000 | 50000 | 10000 | 50000 |
| Petroleum distillate | | | 100000 | 300000 | 100000 | 300000 |
| | | | | | | |
| Measured Concentrations (mg/kg) | | | | | | |
| C ₁ -C ₄ decalins | 81 | | 155.5 | | 155.5 | |
| 2-methylnaphthalene | 10 | | 1.9 | | 1.9 | |
| 1-methylnaphthalene | 6.9 | | 1.3 | | 1.3 | |
| biphenyl | 6 | | 23 | | 23 | |
| C ₂ -C ₄ naphthalenes | 24.1 | | 12 | | 12 | |
| | | | | | | |
| | Surface Application | | Subsurface Injection | | Total | |
| | Corexit 9527 | Corexit 9500 | Corexit 9500 | | | |
| Estimated Mass Loading (kg) | <i>Min</i> | <i>Max</i> | <i>Min</i> | <i>Max</i> | <i>Min</i> | <i>Max</i> |
| 2-butoxyethanol | 243917 | 487835 | | | 243917 | 487835 |
| Proprietary sulfonic acid salt (DOSS) | 81306 | 243917 | 307971 | 923913 | 666003 | 1996008 |
| Propylene glycol | 8131 | 40653 | 30797 | 153985 | 66600 | 333001 |
| Petroleum distillate | | | 307971 | 923913 | 584697 | 1754090 |
| | | | | | | |
| Estimated Mass Loading (kg) | | | | | Total | |
| C ₁ -C ₄ decalins | 66 | | 479 | | 975 | |
| 2-methylnaphthalene | 8 | | 6 | | 19 | |
| 1-methylnaphthalene | 6 | | 4 | | 13 | |
| biphenyl | 5 | | 71 | | 139 | |
| C ₂ -C ₄ naphthalenes | 20 | | 37 | | 90 | |



Table 5: Concentrations of total extractable material (TEM) and the three Corexit marker compounds in the benchtop water soluble fractions (WSFs) prepared and analyzed herein. All concentrations are in mg/L_{water}. TEM concentrations are surrogate corrected; Corexit marker compound concentrations are not surrogate corrected.

| | Corexit 9500 WSF | | Corexit 9527 WSF | | Seawater Blank |
|---|------------------|----------|------------------|----------|----------------|
| | Sample 1 | Sample 2 | Sample 3 | Sample 4 | |
| TEM (C₉-C₄₄) | 4730 | 4220 | 4290 | 4110 | 0.61 |
| Corexit Marker Compounds | | | | | |
| 2-butoxyethanol | 0.003 | nd | 404 | 374 | 0.000 |
| di(propyleneglycol)-n-butyl ethers | 1270 | 1630 | 0.126 | 0.029 | 0.001 |
| Bis-(2-ethylhexyl)fumarate | 0.950 | 1.08 | 1.14 | 1.31 | nd |
| Selected Percentages | | | | | |
| %TEM as 2-butoxyethanol | < 0.1 | nd | 9.4 | 9.1 | < 0.1 |
| %TEM as Glycol Ether Isomers | 26.8 | 38.6 | < 0.1 | < 0.1 | 0.14 |
| %TEM as Bis-(2-ethylhexyl)fumarate | < 0.1 | < 0.1 | < 0.1 | < 0.1 | nd |

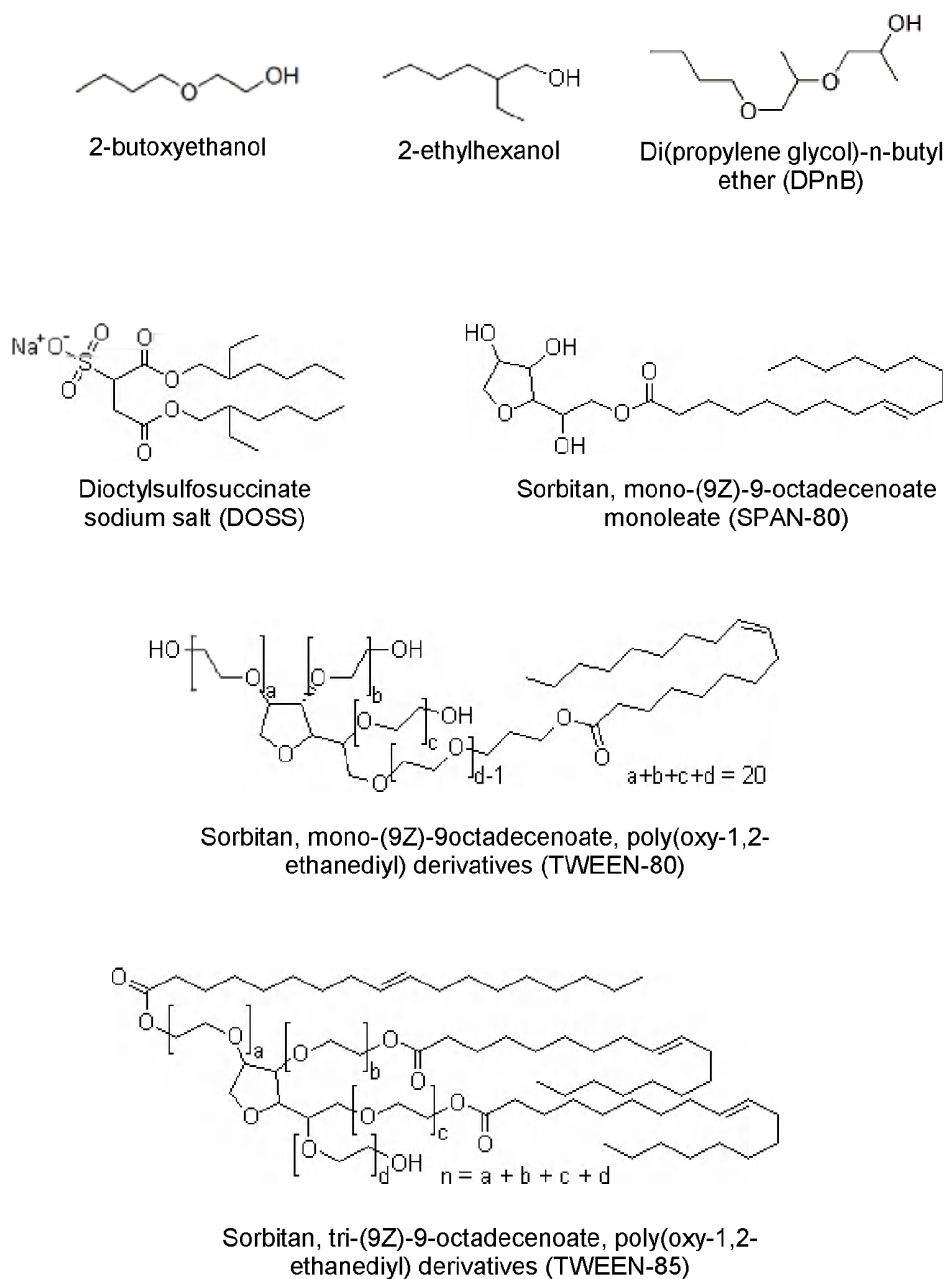


Figure 1: Chemical structures of compounds present in Corexit 9500 and/or Corexit 9527.

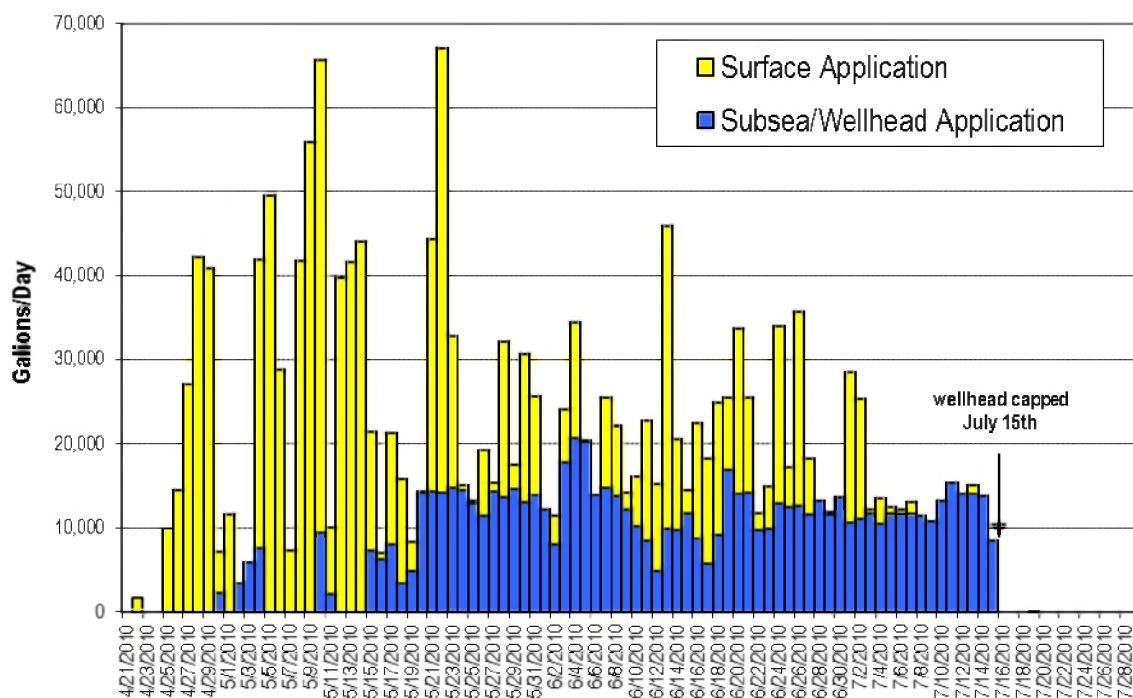


Figure 2: Daily application of dispersants used in response to the *Deepwater Horizon* oil spill. Total surface: 1,073,025 gallons; Total subsea: 771,272 gallons. Data from BP (2014).

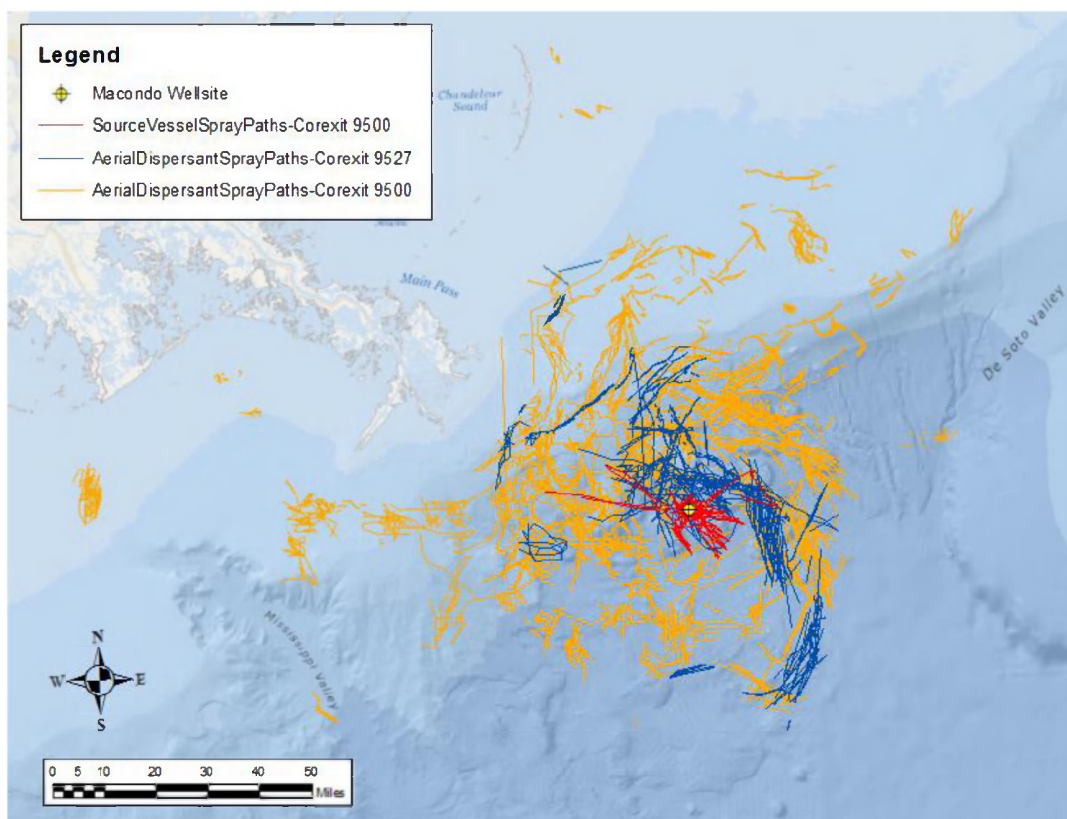


Figure 3: Map showing the extent of aerial and surface vessel applications of dispersants. Data from BP (2014).

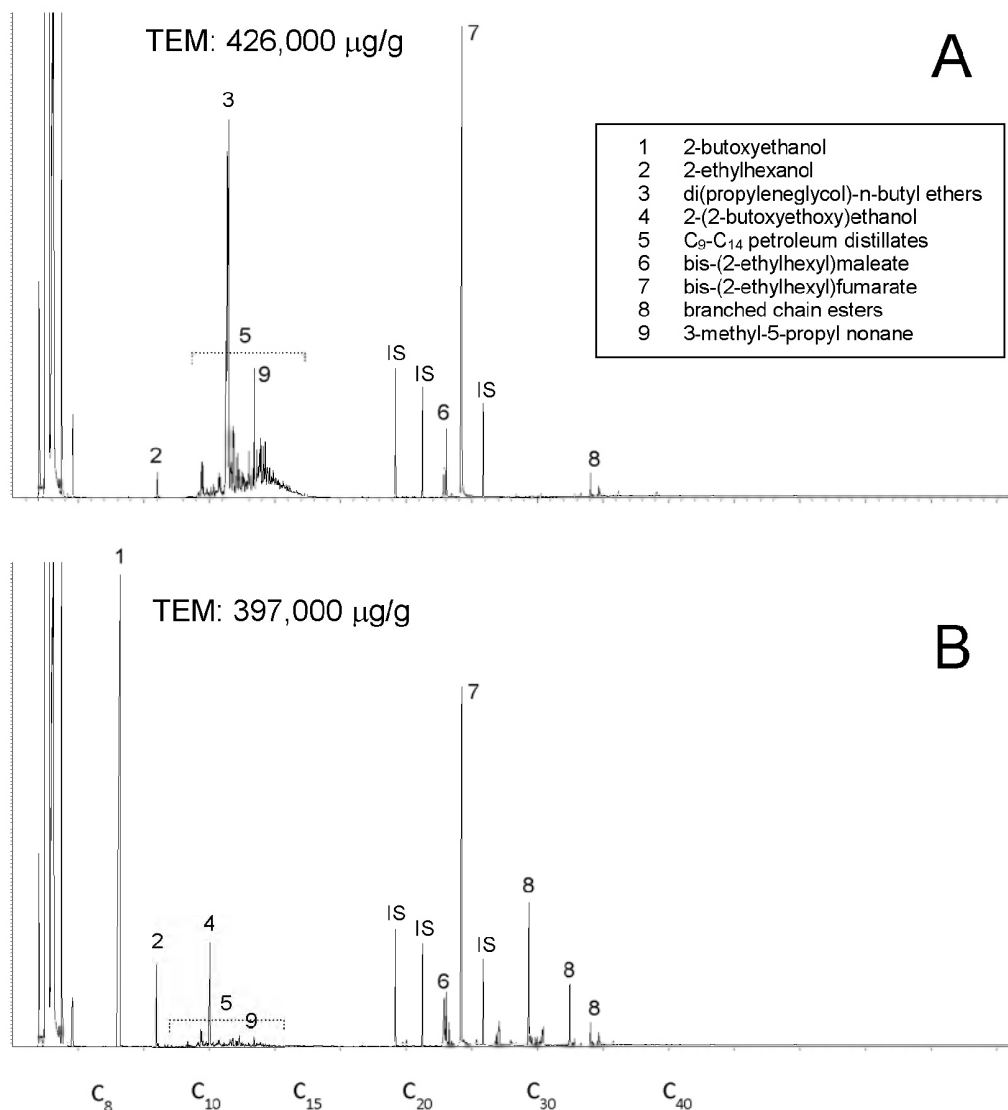


Figure 4: GC/FID chromatograms (C₈+) and total extractable material (TEM) concentrations (µg/g_{dispersant}) for (A) Corexit 9500 and (B) Corexit 9527. IS-internal standard; Key shows peak identities in both formulations as determined by full scan GC/MS.

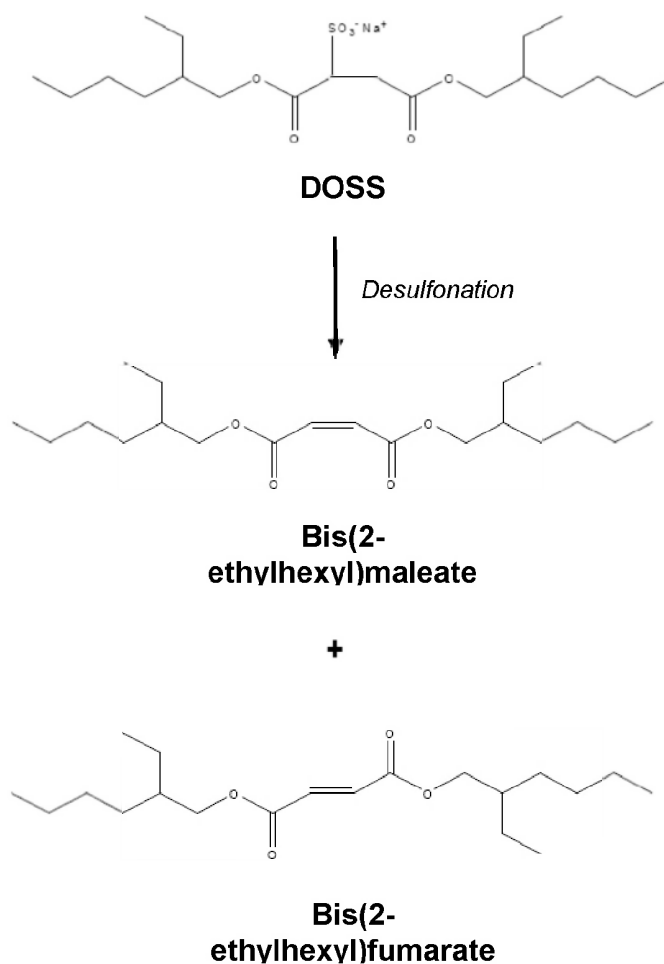


Figure 5: DOSS decomposition (desulfonation) scheme showing formation of maleate and fumarate. Figure provided by Nalco. Desulfonation reportedly occurs upon heating in the injection port of the GC leading to detection of peaks 6 and 7 in Fig. 4.

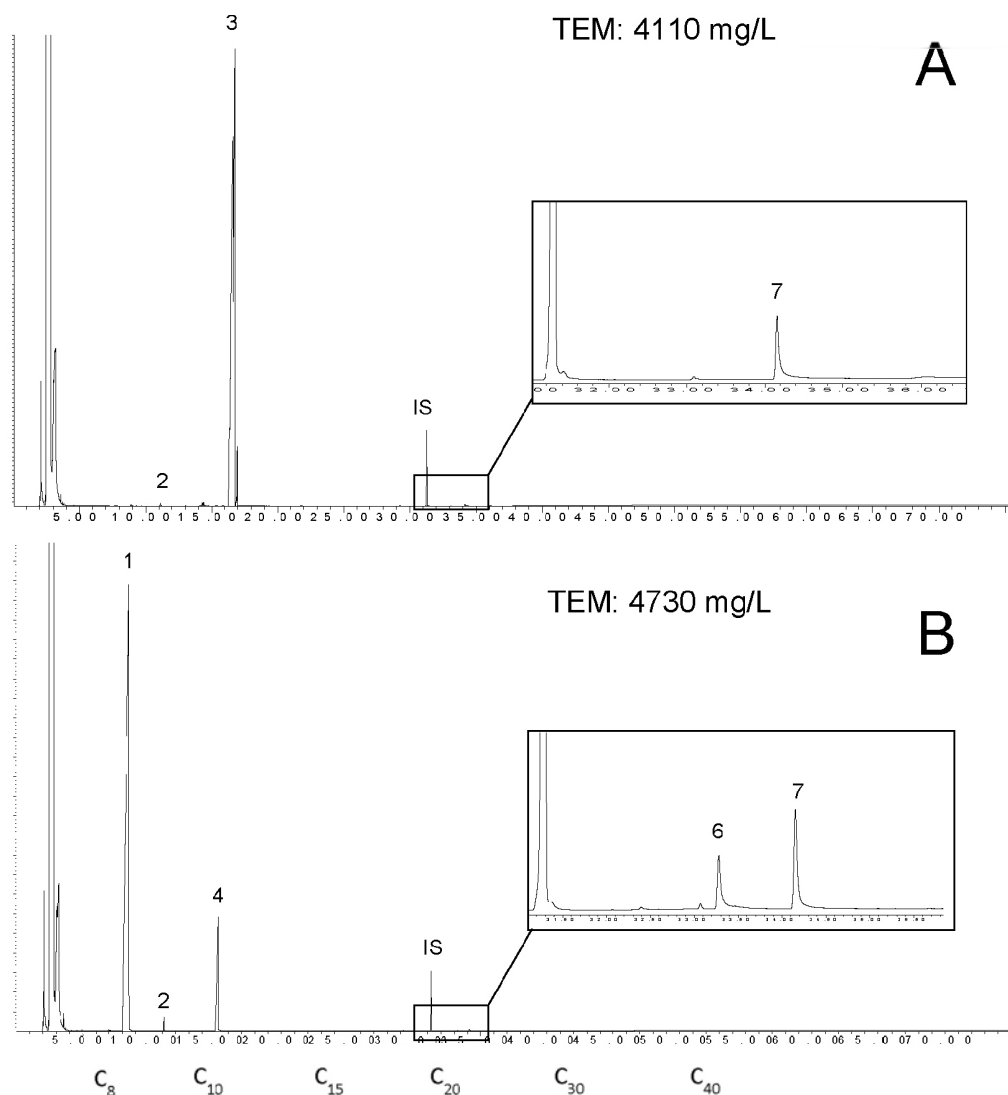


Figure 6: GC/FID chromatograms and total extractable material (TEM) concentrations for (A) the WSF of Corexit 9500 (1007077-01) and (B) the WSF of Corexit 9527 (1007077-03). Insets show expanded views as indicated. IS – internal standard; all other peak identifiers refer to the key in Figure 4.

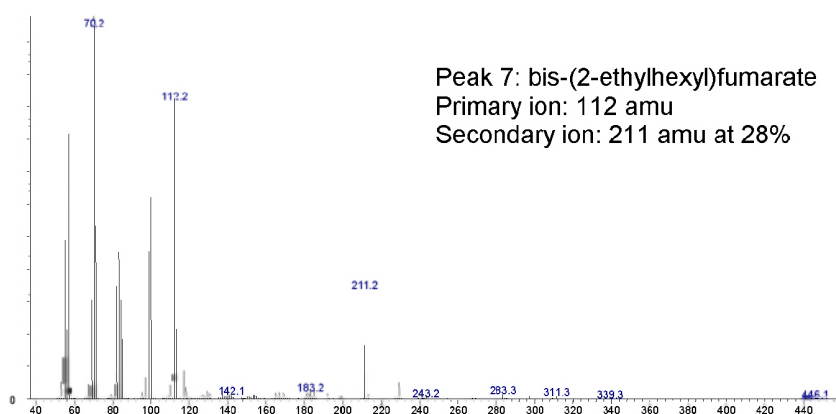
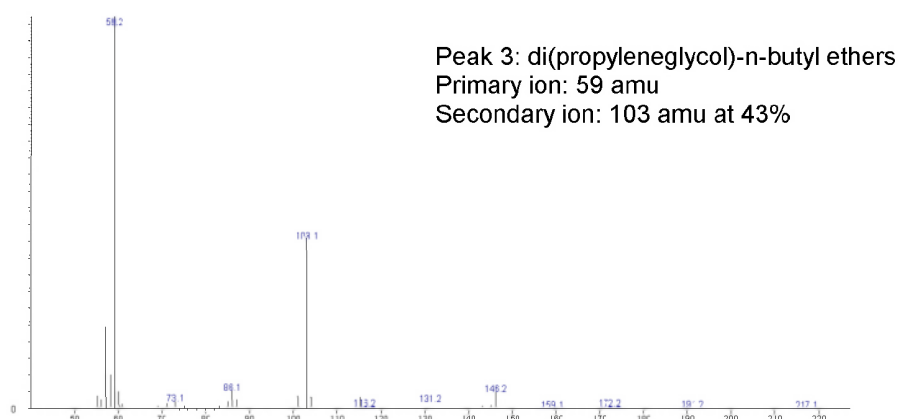
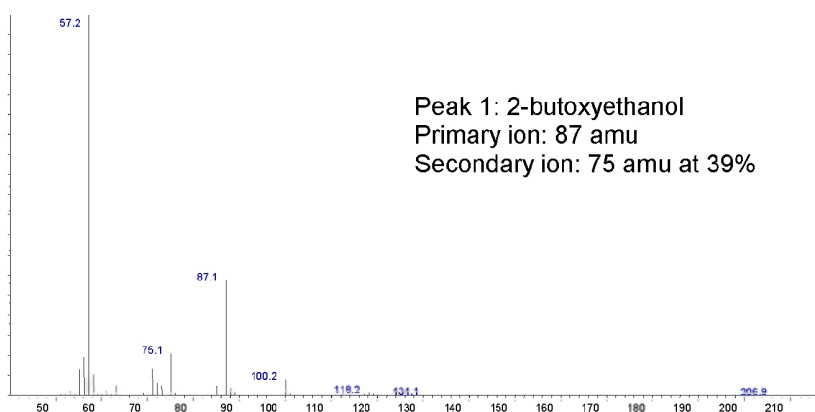


Figure 7: Full scan mass spectra of the three Corexit marker compounds monitored in water samples using GC/MS-SIM.



ATTACHMENTS